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METALLURGICAL AND MATERIALS ENGINEERING

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SUBSTRATES IN THE INITIATION OF HOT
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**INVESTIGATION INTO THE ROLE OF NaCl DEPOSITED
ON OXIDE AND METAL SUBSTRATES IN THE
INITIATION OF HOT CORROSION**

by

N. Birks

SECOND SEMI-ANNUAL REPORT

ON

GRANT NO. NAG 3-44

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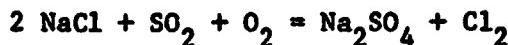
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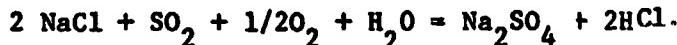
Period Covered: Oct. 1, 1980-April 1, 1981

INTRODUCTION

The conversion of sodium chloride to sodium sulfate in oxidizing atmospheres can occur, whenever the atmosphere contains sulfur dioxide, by two reactions.



and



Sulfur dioxide and water vapor are present in air, especially at low altitude, and in greater concentrations in the combustion gases. Due to the adiabatic compression of air during the compression stage of the gas turbine cycle, at the high pressure end of the compressor temperatures may be achieved allowing the above reactions to proceed. In the combustion chamber the reactions involve mainly the vapor species while any sodium chloride particles surviving passage through the combustion chamber may deposit on stators and turbine blades and convert to sodium sulfate there. In addition any NaCl deposition may cause physical damage to the protective oxide scales existing on the metal surfaces.

In this investigation two aspects are to be studied:

1. The conversion to Na_2SO_4 of NaCl deposited on oxide substrates, as a function of temperature, in air with various SO_2 and H_2O partial pressures. The substrate may be a pure oxide or an oxide scale growing on a metal specimen.

The progress of the reaction will be observed using the SEM-EDAX technique to monitor morphological effects and, as far as possible, establish the rate of the process.

2. The physical characteristics of the interaction between salt and substrate will be studied with particular reference to physical damage to the underlying oxide--especially when this is a scale on a metal specimen - and to chemical interactions. In this respect it is important to establish the conditions under which liquid phases may form and the mechanisms by which they form.

EXPERIMENTAL TECHNIQUES

The first report of this contract contained a description of apparatus and its operation (1). However, for completeness a short description is repeated here.

The apparatus is illustrated in Figures 1 - 4 which are largely self explanatory.

Pure sodium chloride is ground and sized in a dry box and dropped on to the surface of a sample held at temperature within the furnace. The salt sample is injected into the furnace atmosphere using a short burst of nitrogen. The furnace atmosphere consists of air with a predetermined level of SO_2 . Both the furnace atmosphere and the nitrogen are thoroughly dried to exclude moisture.

After the salt has been in contact with the substrate for a predetermined time the specimen pedestal is withdrawn to the cool zone of the reaction tube. The specimen is then removed and transferred immediately to a dried dessicator and is subsequently examined using the SEM-EDAX technique.

Accurate positioning of the hot zone is ensured by the moveable furnace and the controller used allows a set temperature to be maintained to within $\pm 2^\circ\text{C}$.

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Since the presence of water vapor in the atmosphere is expected to influence the reaction the preparation of samples and execution of the experiment is carried out under 'dry' conditions using dry boxes made of perspex and dried by P_2O_5 or $MgClO_4$.

In order to study the effect of moisture, provision has been made for the gas forming the furnace atmosphere to bubble through a water bath, the water vapor content being measured subsequently in a chamber containing a thermometer and humidity meter, in this way H_2O can be added to read 40% relative humidity at 20°C, corresponding to a water vapor partial pressure of 7.65 mm or about 1%, by bubbling the gas through an ice-water mixture at 0°C.

The apparatus is now complete and fully operational. The results obtained so far will be described below.

RESULTS

The apparatus and technique have functioned extremely well benefiting from the very simple design. The only difficulty experienced has been that of controlling precisely the amount of NaCl delivered to the specimen. However, in each case sufficient has remained on the specimen surface for the experiment to be successful. Another pleasing aspect is that so far no damage to the silicaware employed in the hot zone has been observed, there is no apparent change in color or clarity. This may be due to the relatively low temperatures at which the experiments are carried out, clearly the salt particles are either adhering to the specimen or falling to the bottom of the furnace tube. Should any particle stick to the silica tubing then damage due to eventual formation of the low melting sodium silicate would be expected, so far this has not arisen.

4

As might be expected the ground and sized NaCl particles are angular reflecting the cubic crystal and its fracture by cleavage. Figure 5 shows such particles which were hand ground using an agate mortar and pestle in a dry box, then sized between 170 and 200 mesh. The 170/200 mesh particles are about 100 microns in size. Although reasonably uniform, some small fragments are also included in the sample, which is inevitable.

Figure 6 shows the surface of an alumina substrate disc freshly prepared using a diamond cutting wheel before exposure. This is included for comparison with the substrate areas in between NaCl particles after reaction has occurred.

In the period reported upon samples were exposed for times of 10, 30, 60, 120 and 240 minutes at temperatures of 500 and 600°C in atmospheres of air containing 0.2% and 1% of SO₂. After exposure the sample surfaces were examined using the SEM-EDAX technique. Particles of nominal 100μm dimensions (Figure 5) were used for this stage of the investigation corresponding to the initial stage shown in the block diagram of the whole program which is appended.

RESULTS AT 500°C

(a) 0.2% SO₂

Figure 7 shows the initial salt particle after exposure to this atmosphere for 120 minutes. EDAX analysis show that only a trace of sulfur is detectable on the particle surface which is still predominantly sodium chloride. The trace of aluminum indicated is puzzling and requires re-examination to establish whether it is real or an artifact. If it is real it may indicate the participation of a vapor species containing aluminum in the reactions. After 240 minutes exposure substantially the same results were obtained indicating that the reaction is slow at 500°C.

Although the alumina substrate appears to be unchanged in Figure 7b, a higher magnification (x1400) shown in Figure 7a reveals some detail on the surface which could be the initial stages of a deposit. This specimen will be reexamined to investigate this feature.

(b) 1% SO₂

Specimens were exposed to this atmosphere for times up to 240 minutes. Even after 240 minutes the appearance of the specimen showed evidence of only slight reaction (Figure 8). Consequently more detailed examination using EDAX was deferred and subsequent experiments were carried out at 600°C.

RESULTS AT 600°

(a) 0.2% SO₂

10 Minute Exposure

Figure 9 shows detail of a typical salt particle and the accompanying EDAX gives no indication of the presence of sulfur. Similarly the alumina substrate showed no sign of change until examined at X4000 when tiny globules were evident on the alumina surface. These are shown in Figure 10. The corresponding EDAX results show that the globules contain sulfur and sodium compared with the alumina surface alongside which is virtually free of these elements.

30 Minute Exposure

More reaction appeared to have taken place as shown in the SEM micrograph of Figure 11. The corresponding EDAX shows a surprisingly low indication of sulfur however and this specimen will be reexamined. The reaction appears to have initiated at discrete sites on the NaCl surface and to produce a relatively porous reaction product.

120 Minute Exposure

So far as EDAX indications are concerned only a very small trace of chlorine is shown on the particle according to Figure 12. Of course this does not penetrate to be centre of the particle and indicates that the surface layer is likely to be composed entirely of sulfate. As shown in Figure 12 the sulfate nucleated at discrete sites has grown to provide a porous, nodular surface coverage to the original salt particle. The alumina substrate is also covered with a deposit which has still to be investigated and identified.

240 Minute Exposure

Figure 12 shows both the particle and the alumina substrate to be covered with a layer of growth nodules. The EDAX responses from the particle shows strong sulfur and chlorine peaks indicating that conversion to sulfate is well advanced. The EDAX response from the substrate shows strong sodium and sulfur peaks with no indication of chlorine. The very strong aluminum peak in this case confirms that the analytical electron beam is penetrating the surface layer through to the substrate. It can be concluded therefore that the surface layer consists of sodium sulfate only and that chloride is absent.

These impressions are confirmed by examination of the substrate at higher magnification shown in Figure 14.

(b) 1% SO₂

10 Minute Exposure

Even after 10 minutes substantial reaction has occurred. Figures 15 and 16 show the presence of both sulfur and chlorine in both the salt particle and the substrate with comparable strengths of the characteristic x-rays of both elements.

In another area the surface of the salt particle is pitted with sites which are shown by x-ray imaging, in Figure 17, to be sulfate nucleation and growth sites. Apparently particles on the same specimen do not react at the same rate. The reason for this is not known.

30 Minutes Exposure

Similar reaction has occurred with deposit observed on both salt particle and substrate. On this specimen a new feature was seen or shown in Figure 18. The salt particle observed in this Figure was adjacent to other sites from which the salt had either evaporated or fallen off. A curious feature is that the substrate in this region showed only very low sulfur EDAX response and no chlorine peak, although higher magnification revealed the presence of small nodules on the surface.

The salt crystal itself is well covered and gives strong EDAX indications of sodium, sulfur and chlorine with a faint aluminum response as shown in Figure 19.

Figure 20 shows a higher magnification of the substrate and superimposed EDAX traces shows the presence of sulfur and sodium from the growth crystal (trace B dotted) but no sodium or chlorine from the substrate (trace A full). A high magnification shows the growth nodules to be strongly crystalline.

60 Minutes Exposure

In this case the salt particle shown has not been attacked uniformly and the part illustrated in Figure 21 shows areas devoid of sulfate. The small crystalline growths are evidently sodium sulfate, according to the EDAX response.

240 Minutes Exposure

The appearance is similar to that of the previous specimen with many isolated sulfate growths, although on the corners and edges of the salt particle a coherent fairly solid and compact sulfate layer appears to be forming as illustrated in Figure 22.

Discussion

The results reported above have so far been partly exploratory and several exposure conditions will be repeated to establish the extent to which results can be reproduced. Certain specimens also require further examination in the light of the features revealed in other samples.

The main observation so far is that all of the specimens examined so far have certain common features. Sodium sulfate nucleates in each case at isolated centers and grows until they impinge and form a surface layer that appears to be porous. In each case also the alumina substrate becomes covered with isolated globules of sodium sulfate which proceed to grow and eventually cover the substrate surface with what also appears to be a porous layer.

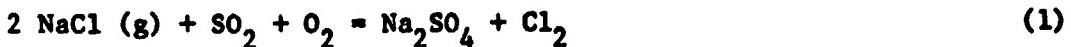
The conversion of sodium chloride to sodium sulfate therefore proceeds by two mechanisms, the *in situ* conversion of the original salt particle and the formation of sulfate on the substrate by reaction of NaCl vapor with SO₂ and O₂ in the atmosphere nucleating or depositing at discrete sites on the alumina substrate. A diagrammatic interpretation of these mechanisms is given in Figure 23.

The relative contributions of the two mechanisms to the overall reaction will depend upon the value of the vapor pressure of sodium chloride. If P_{NaCl} is low then most of the reaction will occur on the original salt

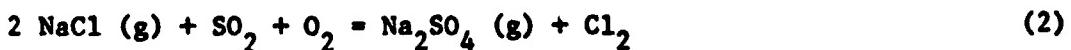
surface. At higher temperatures, when P_{NaCl} is higher, a larger fraction of the total reaction will occur on the alumina substrate.

The nature of the Na_2SO_4 layer formed is also important since the formation of an impervious layer would stop the evaporation of the NaCl and confine the reaction to the original salt surface. So far the evidence points to the formation of a porous layer predominantly, although on the edges and corners of a few specimens evidence of a compact reaction product has been found as shown in Figure 22.

One question that is difficult to comment upon is whether the sodium sulfate deposited on the alumina substrate actually forms there by direct reaction from the gas phase according to



An alternative mechanism would be the formation of Na_2SO_4 in the gas phase followed by deposition from the vapor according to



and



Methods of evaluating these two possibilities by experiment and calculation will be considered in the future program.

It is also noticeable that, at 600°C, the amount of sulfate formed on both surface and substrate does not appear to be as great as might be expected from the appearance of specimens exposed for short times. Certain experiments will be duplicated in order to check whether or not reproducible conditions are being obtained.

The reaction appears to have started more rapidly at 600°C than at 500°C as might reasonably be expected

These initial results also indicate that increasing the SO_2 content from 0.2 to 1% did not produce any marked increase in reaction rate either at 500 or 600°C. Thus the reaction rate appears not to be limited by the supply of SO_2 from the gas phase.

CONCLUSIONS

The apparatus and the experimental technique appear to be working very well according to the initial results reported here. Several confirmatory experiments will be carried out to substantiate the reproducibility of the technique.

The conversion of sodium chloride to sodium sulfate can be observed easily using the SEM-EDAX technique. It proceeds by two mechanisms involving (a) direct *in situ* conversion and (b) deposition of sulfate on to the surrounding substrate probably following a vapor phase reaction subsequent to the evaporation of NaCl from the particle.

Quantitative measurements of reaction kinetics have not, so far, been possible.

FUTURE WORK

The next experiments will consist of repeating selected conditions to determine the reproducibility of the results obtained so far. Several specimens also require reexamination to establish the nature of the deposit formed on the subscale.

The program will then be to widen the range of conditions examined. This will involve increasing the temperature to 650 and 700°C and making a close study of the formation of liquid phases from the $\text{NaCl-Na}_2\text{SO}_4$ system, the morphology of the liquid phase formed on the substrate and whether it interacts with the substrate.

Attempts will be made to expose single NaCl crystals large enough to fracture or section in order to examine the NaCl-Na₂SO₄ interface and by measuring the thickness of both crystal and reaction product layer, obtain some measurement of reaction kinetics.

The effects of additions of water vapor to the air atmosphere will also be studied and, to this end, a gas train for water addition and water vapor pressure measurement has already been installed.

Eventually interactions with oxides grown as metal substrates will be studied as indicated in the accompanying block diagram of the program.

STAFFING

Mr. C. T. Kang has now left this program to undertake work on erosion and corrosion interactions on metals at high temperatures. He will retain an interest since he will be the SEM-EDAX operator for this program and here his previous association will be invaluable.

Mr. M. Miller, a Junior Undergraduate has taken over the experimental side of the project under Dr. N. Birks. Mr. Miller is an enthusiastic and extremely capable student and the program is not expected to lose pace.

References

1. N. Birks, First Semi Annual report on NAG 3-44 covering Apr. 1 - Oct 1, 1980,
"Investigation of the role of NaCl deposited on oxide and metal substrates
in the initiation of metal substrates."

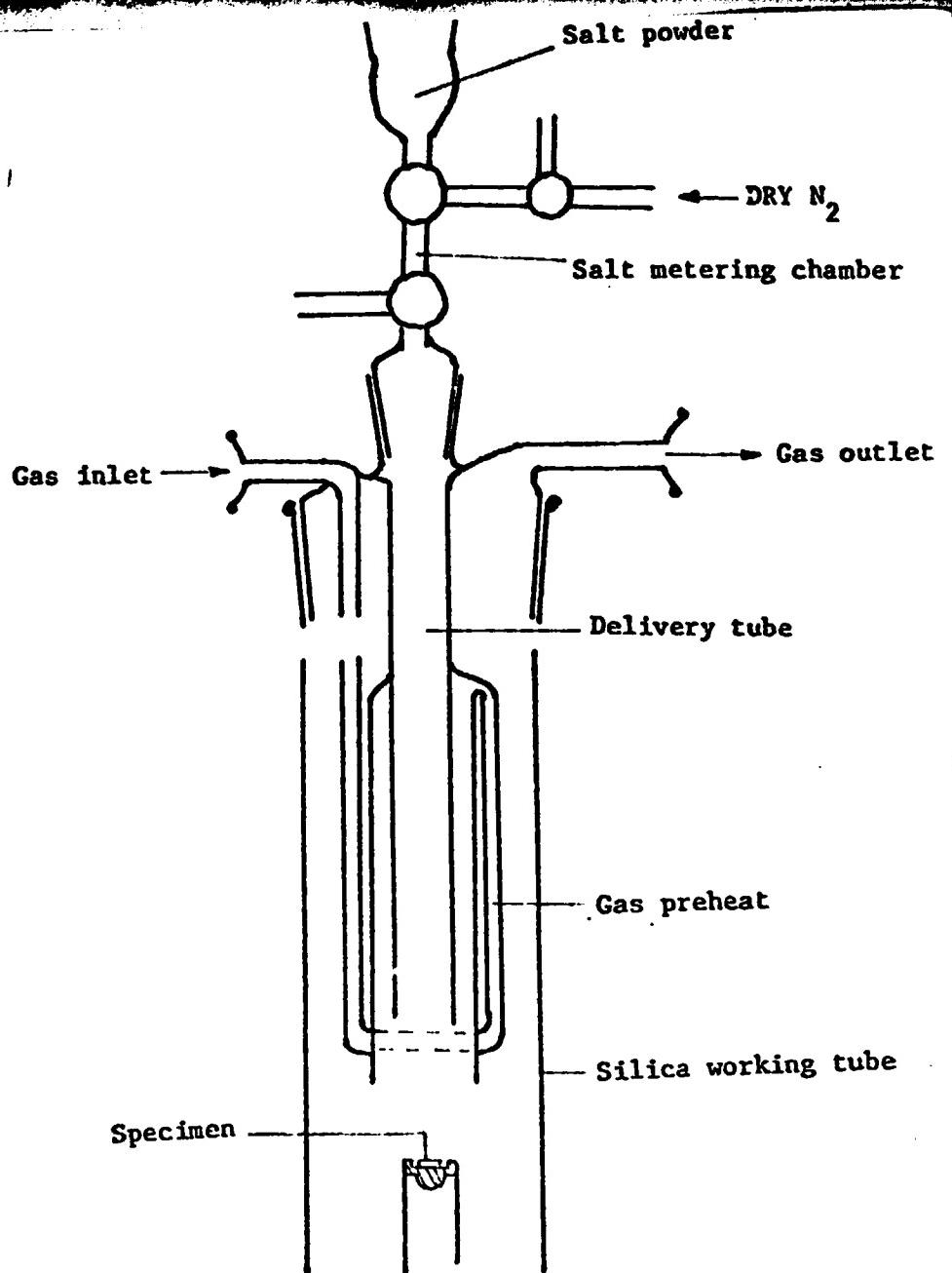
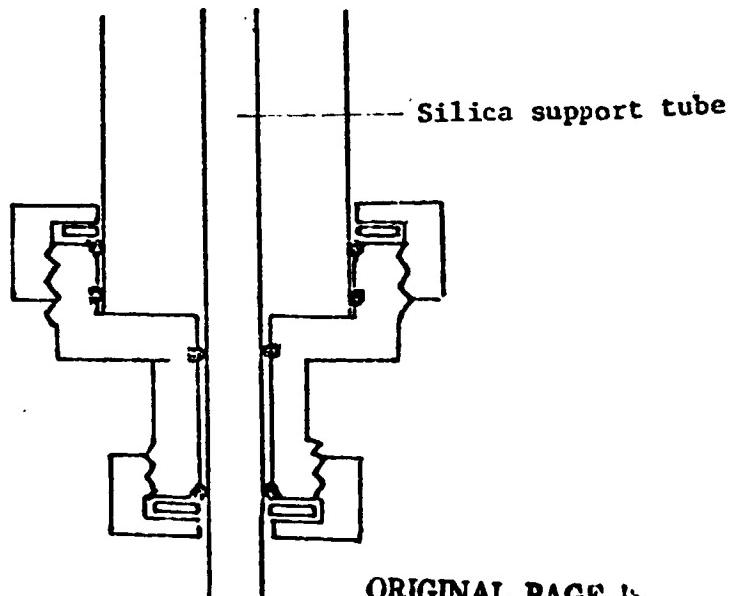


Figure 1

Diagram of apparatus for gas
 preheat and delivery of dry,
 sized, NaCl powder on to a
 substrate held at temperature.



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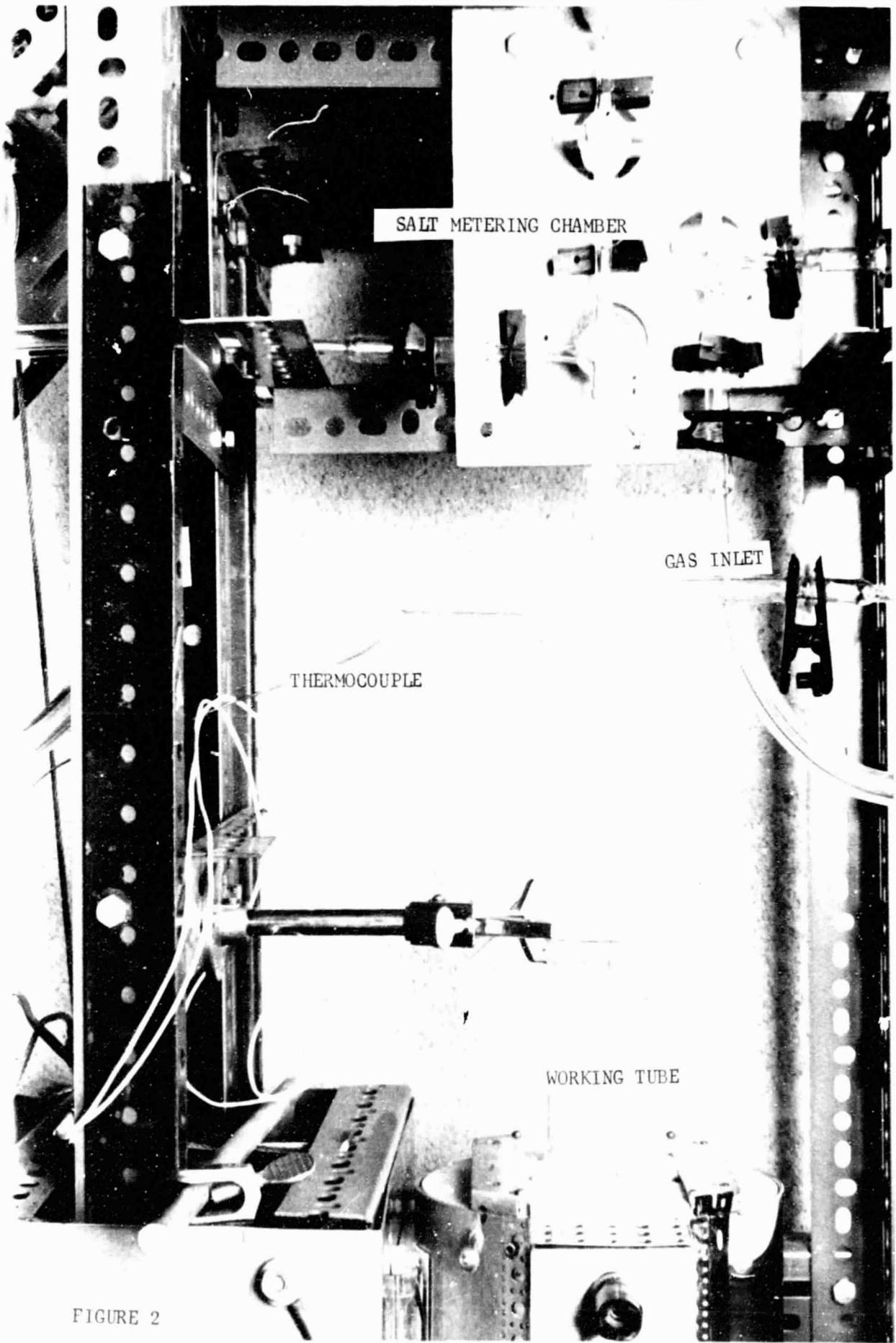


FIGURE 2

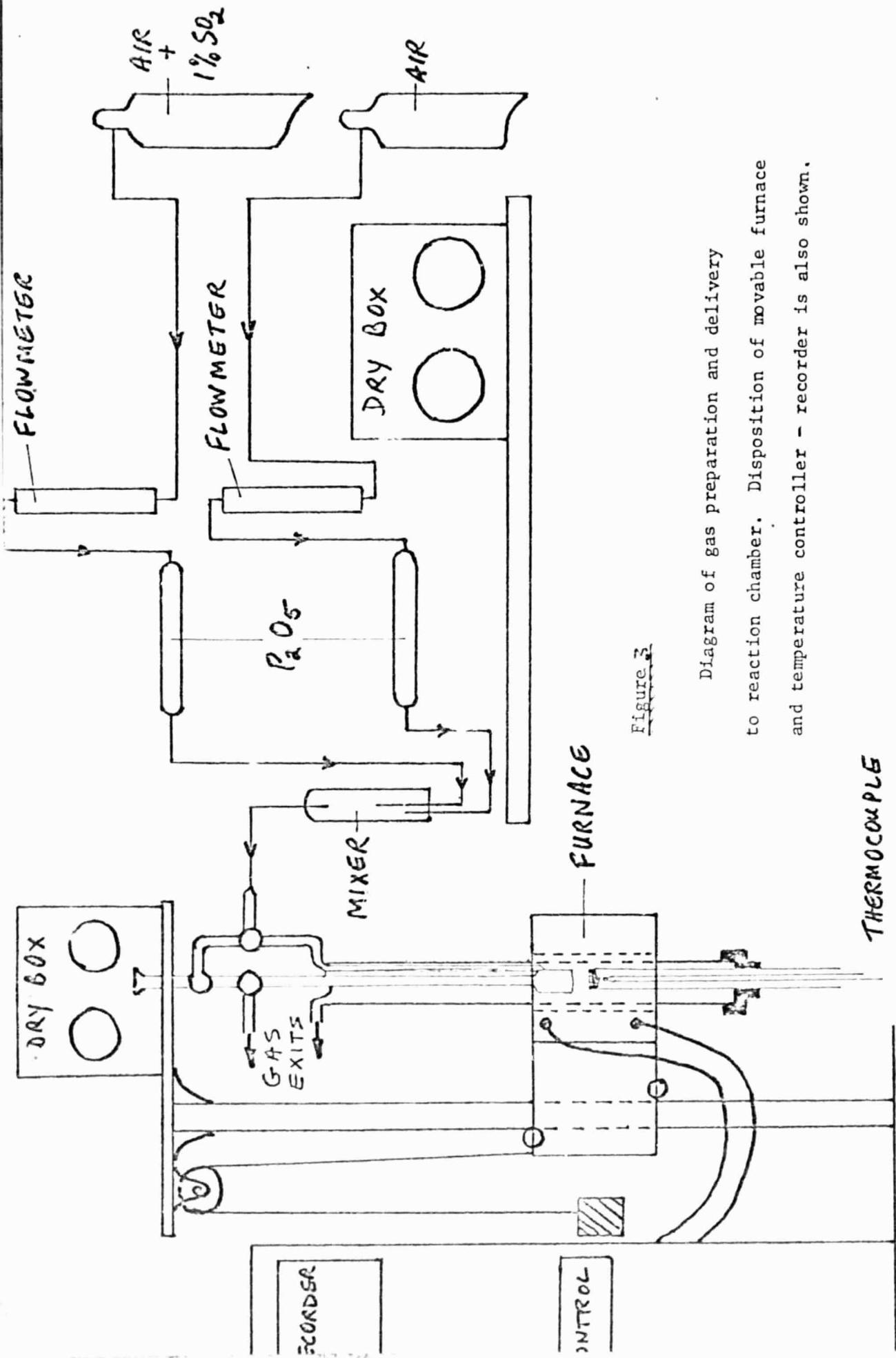


Diagram of gas preparation and delivery
to reaction chamber. Disposition of movable furnace
and temperature controller - recorder is also shown.

Figure 3

THERMOCOUPLE

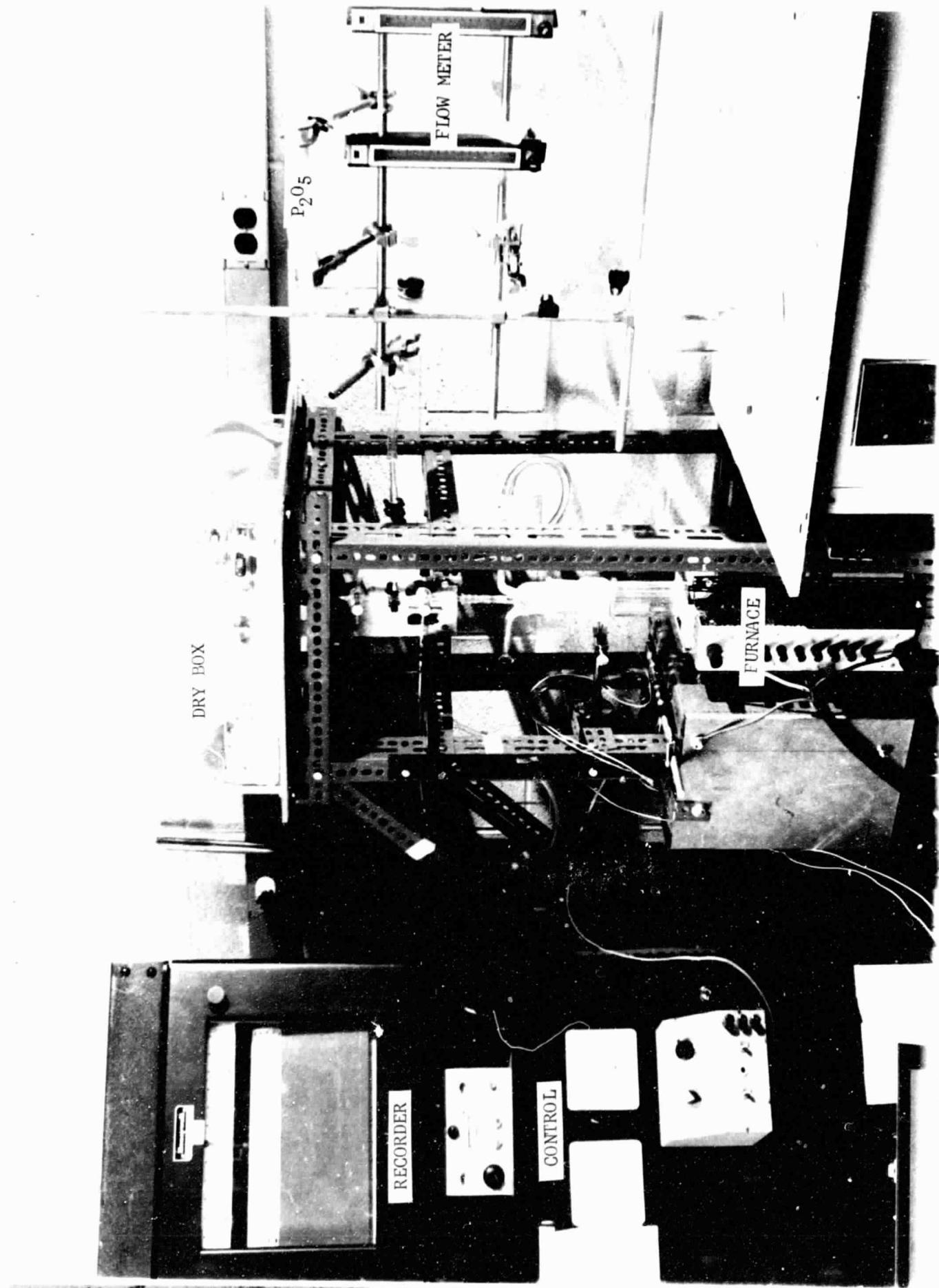
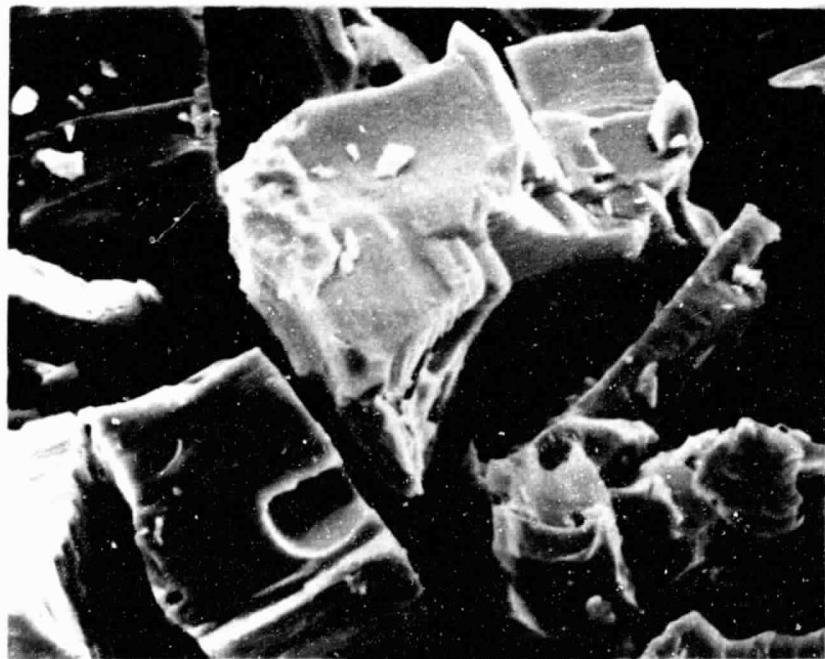


FIGURE 4



a.) X 140

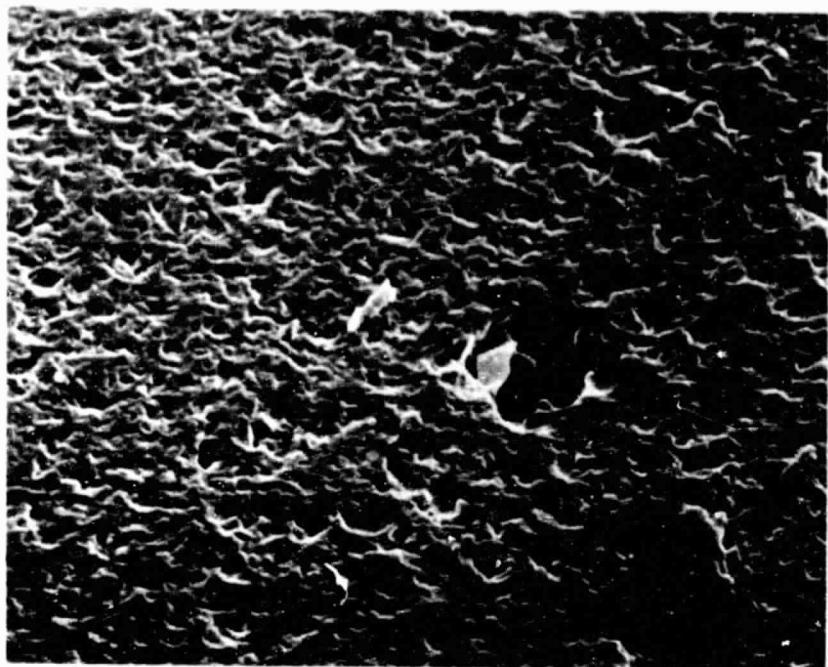


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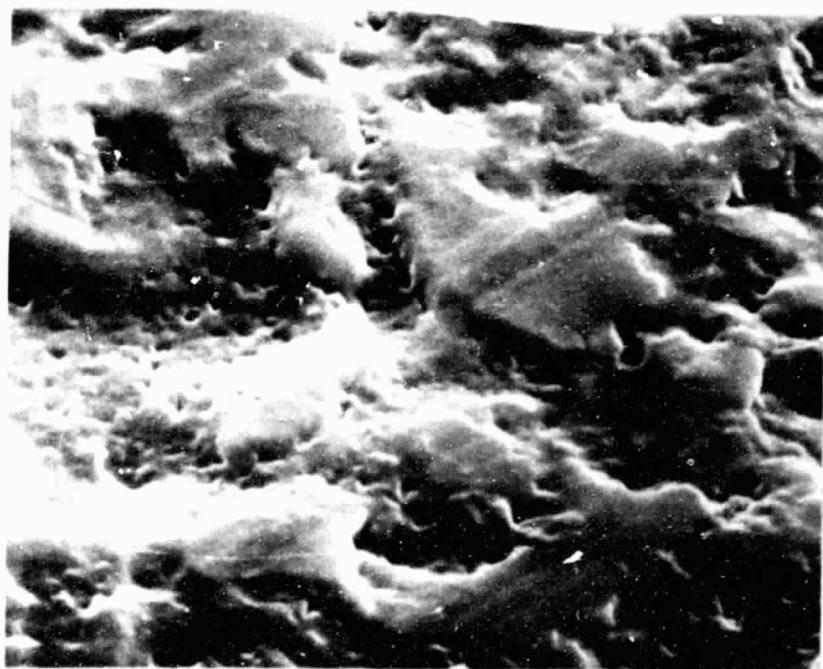
b.) X 700

NaCl PARTICLES GROUND TO 170/200 MESH.

FIGURE 5



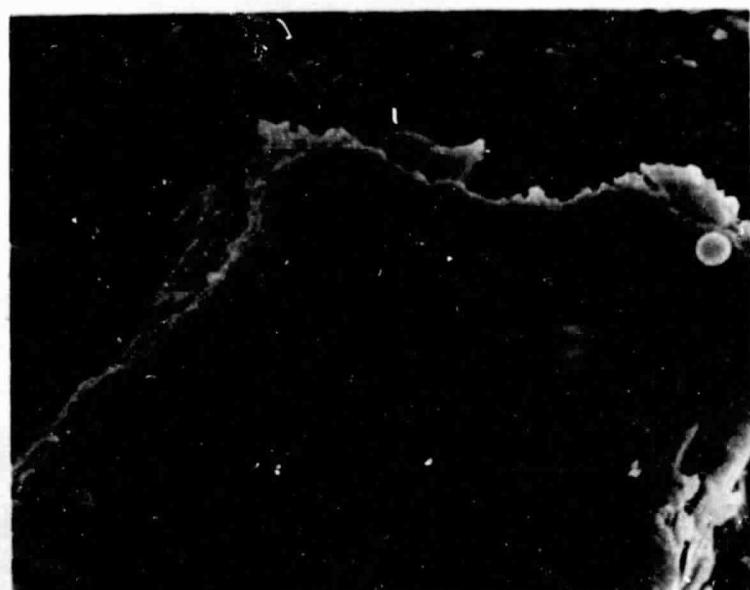
a.) X 375



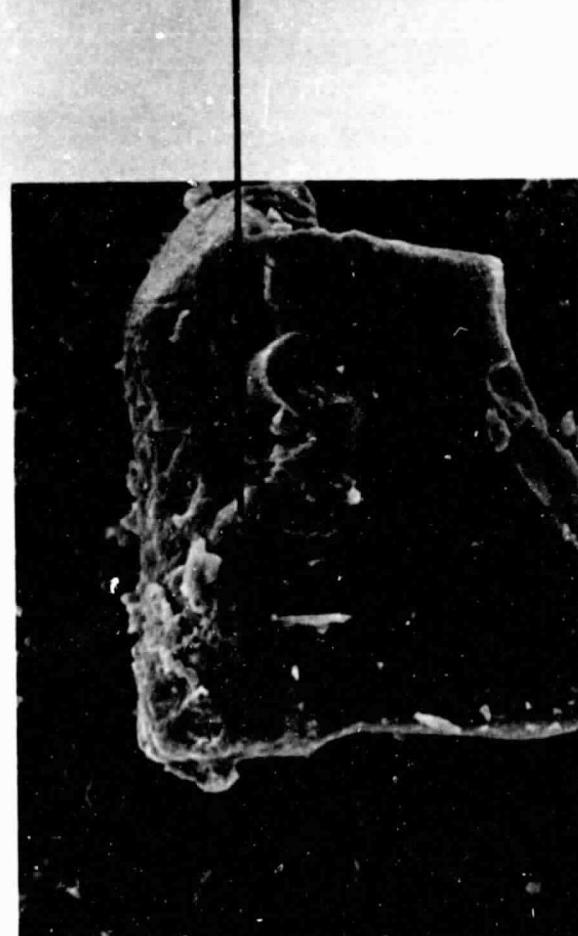
b.) X 1430

SURFACE OF Al_2O_3 SUBSTRATE DISC FRESHLY SECTIONED WITH A DIAMOND CUTTER.

FIGURE 6

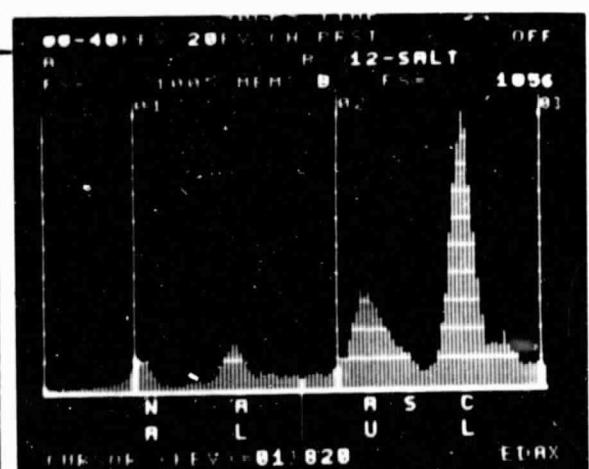


a.) X 1400



b.) X750

EDAX OF NaCl PARTICLE;
TRACE OF SULFUR PRESENT.

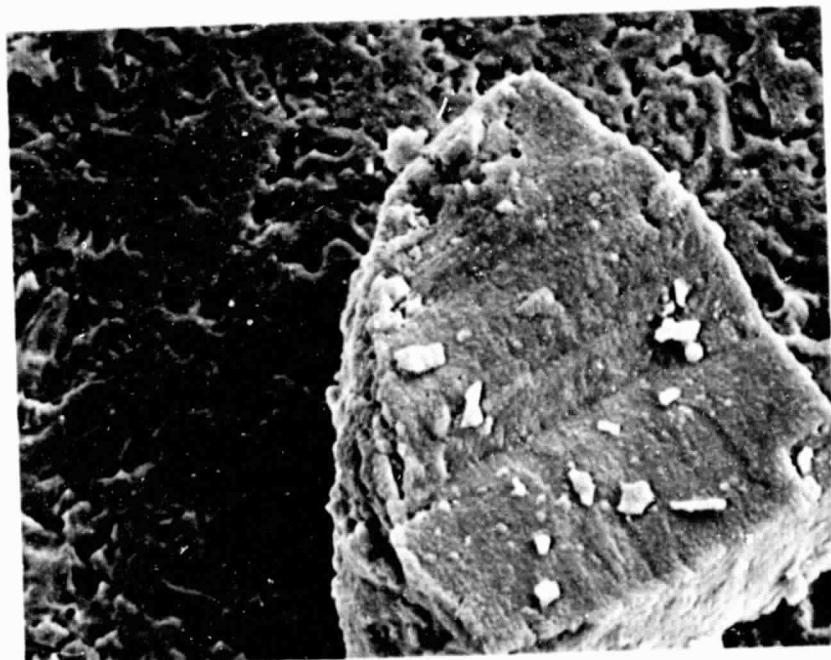


NaCl PARTICLE EXPOSED TO AIR PLUS 0.2% SO₂ AT 500° C. FOR TWO HOURS.

FIGURE 7



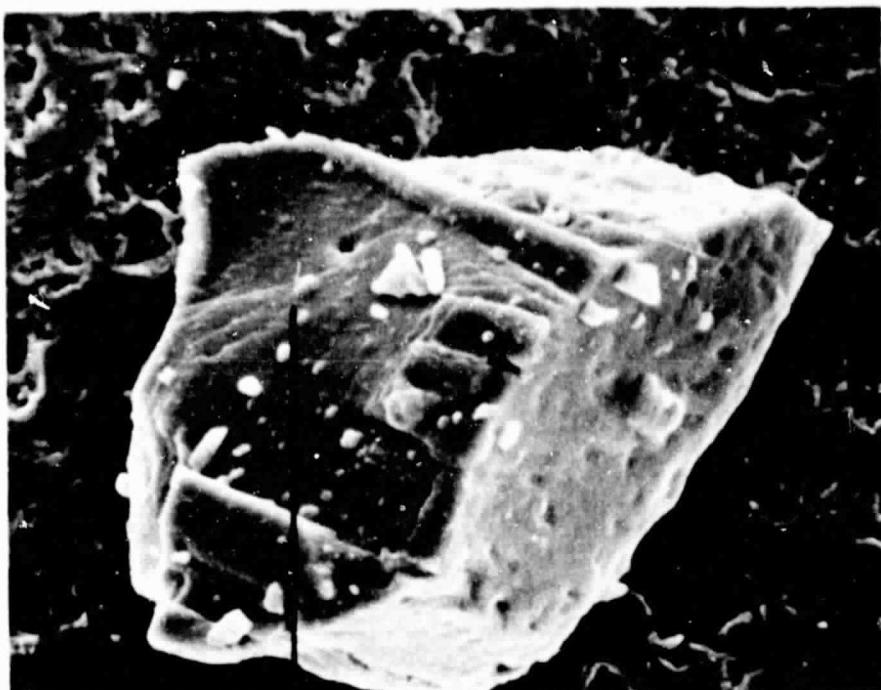
a.) X 800



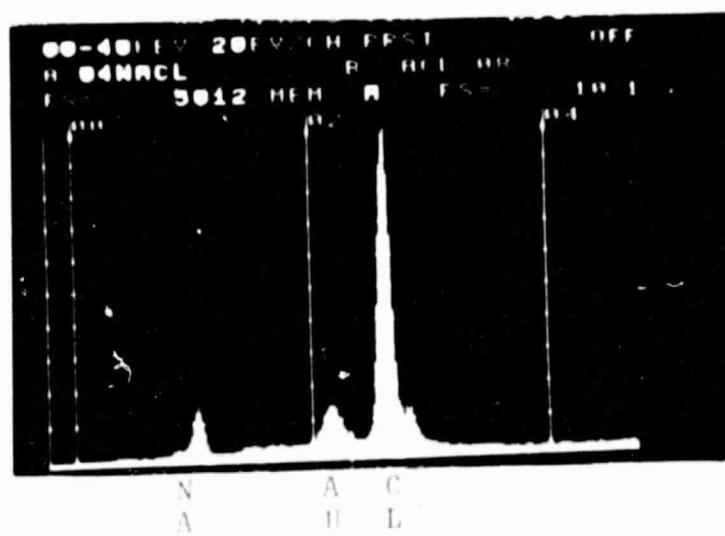
b.) X 800

NaCl PARTICLES EXPOSED TO AIR AND 0.99% SO_2 AT 500^0 C . FOR FOUR HOURS.

FIGURE 8



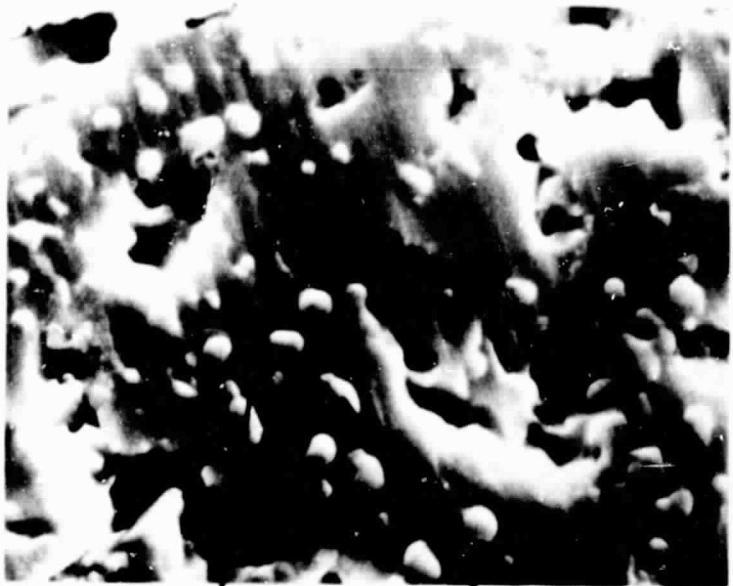
X 800



EDAX OF NaCl PARTICLE:
NO SULFUR PRESENT.

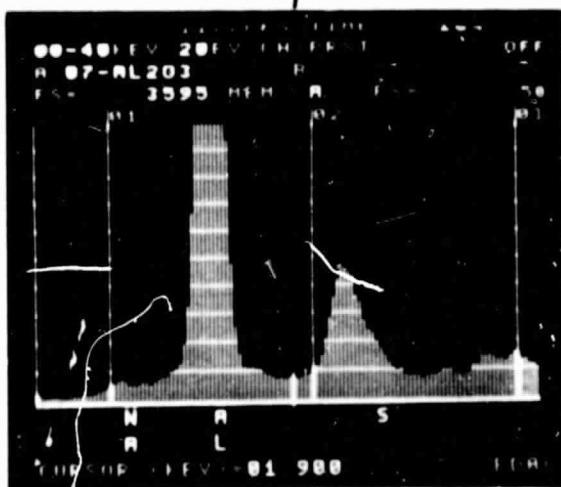
NaCl PARTICLE EXPOSED TO AIR AND 0.2% SO₂ AT 600° C. FOR 10 MINUTES.

FIGURE 9

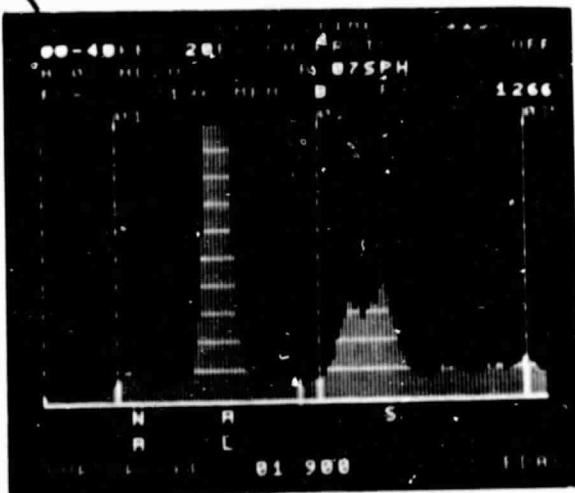


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X 4000



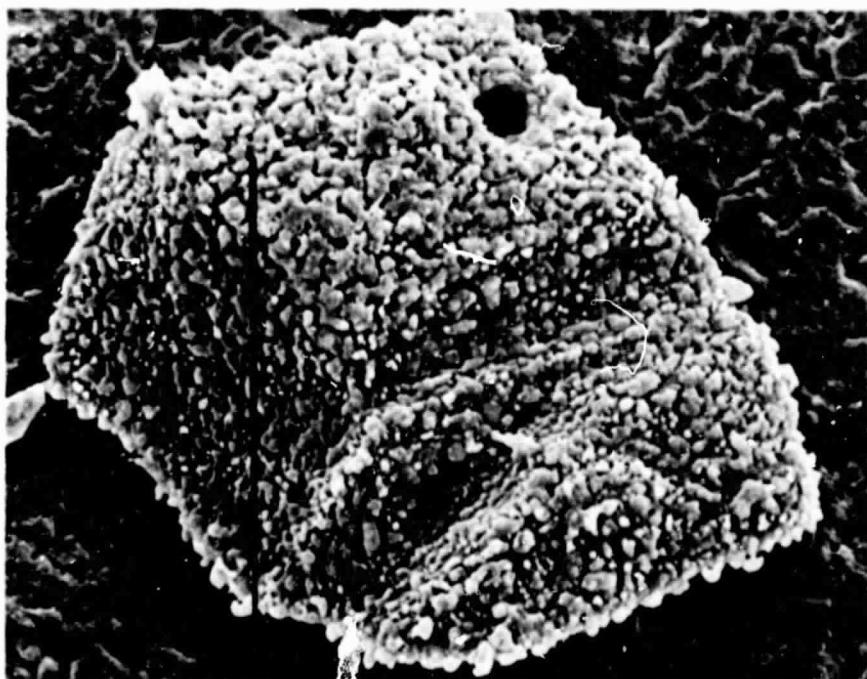
EDAX OF Al_2O_3 SUBSTRATE.



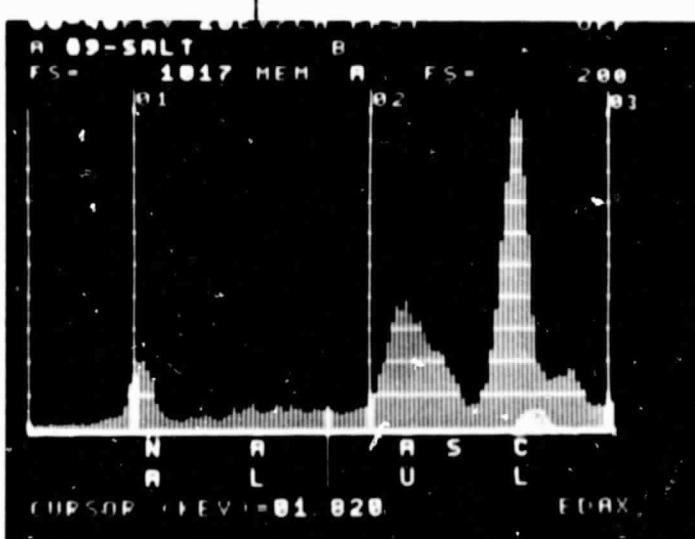
EDAX OF SULFUR-RICH GLOBULES.

Al_2O_3 SUBSTRATE EXPOSED TO AIR AND 0.2% SO_2 AT 600°C . FOR 10 MINUTES.

FIGURE 10



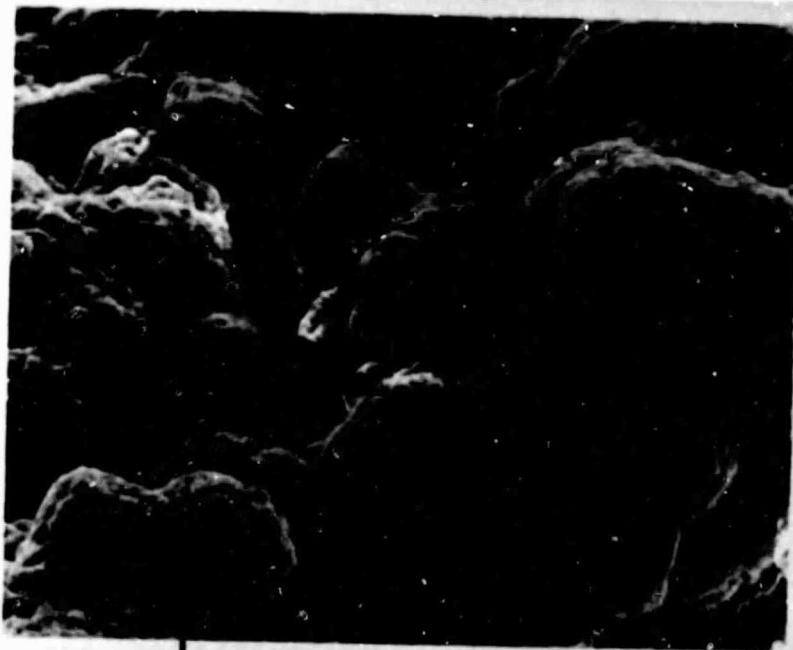
X 750



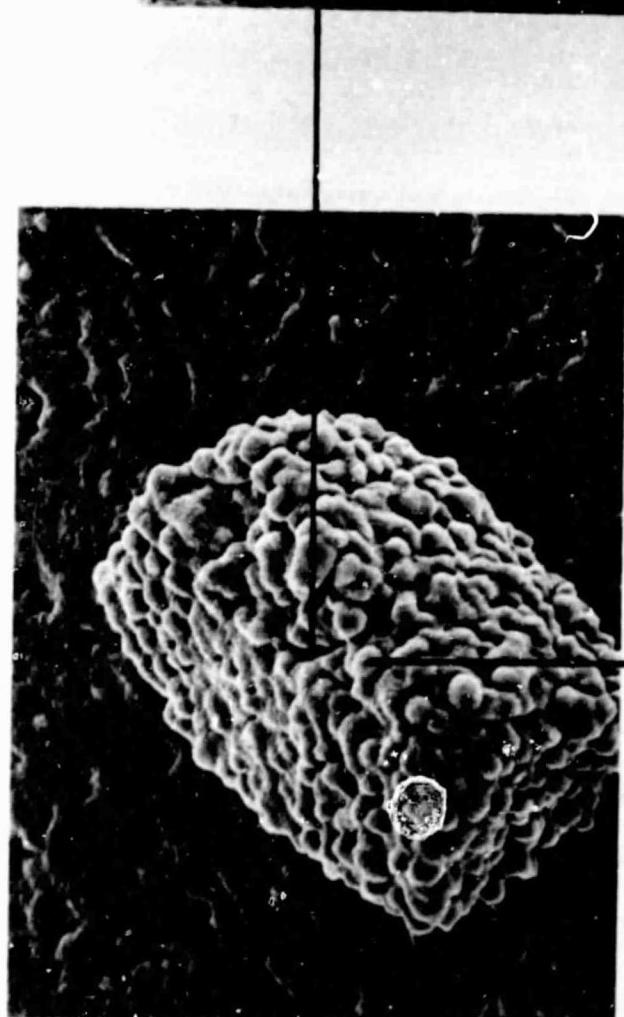
EDAX OF NaCl PARTICLE;
SULFUR PEAK PRESENT.

NaCl PARTICLE EXPOSED TO AIR AND 0.2% SO₂ AT 600⁰ C. FOR 30 MINUTES.

FIGURE 11

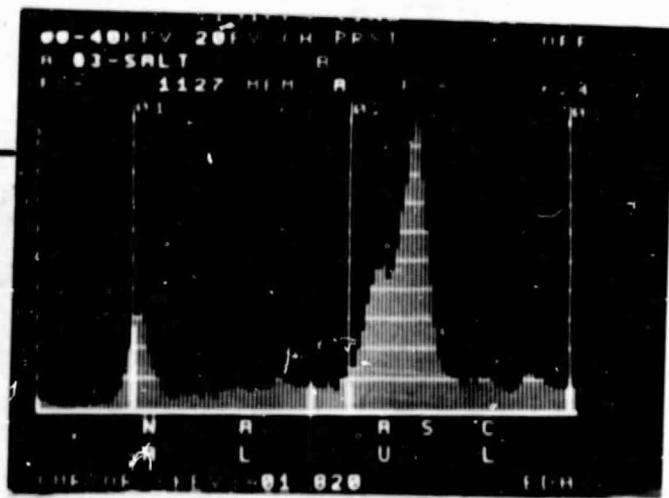


X 3750



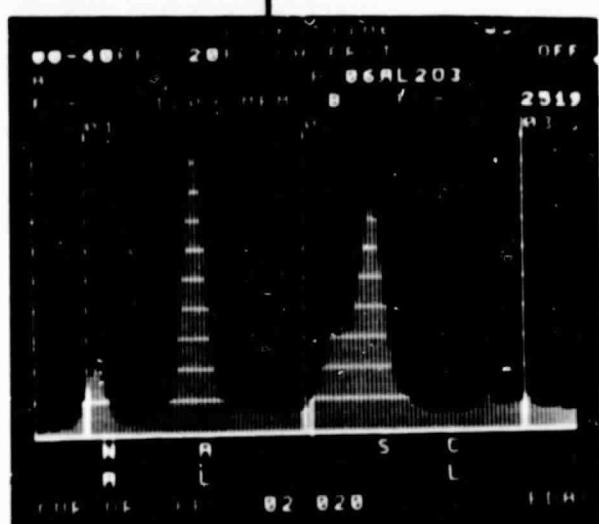
X 750

EDAX OF NaCl PARTICLE;
HIGH SULFUR CONTENT NOTED.

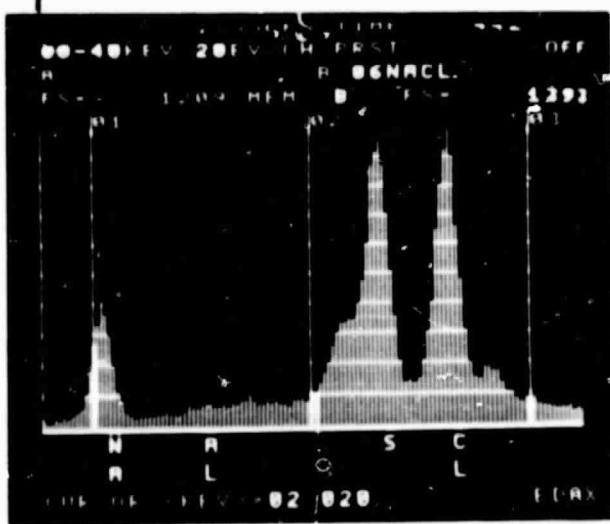


NaCl PARTICLE EXPOSED TO AIR AND 0.2% SO₂ AT 600° C. FOR TWO HOURS.

FIGURE 12



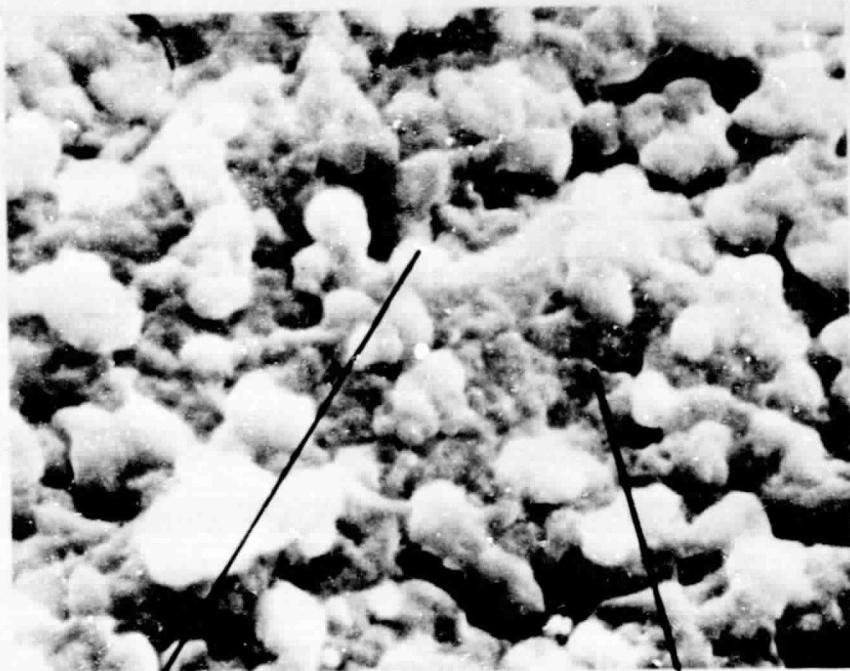
EDAX OF Al_2O_3 SUBSTRATE;
NO CHLORINE PEAK.



EDAX OF NaCl PARTICLE;
SULFUR AND CHLORINE PRESENT.

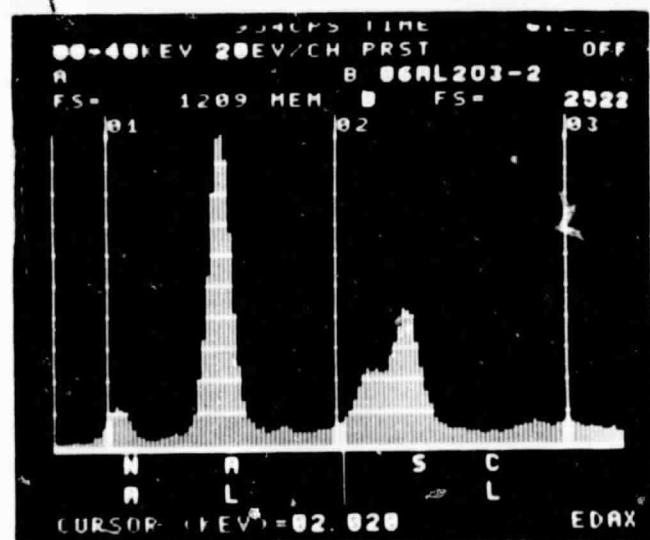
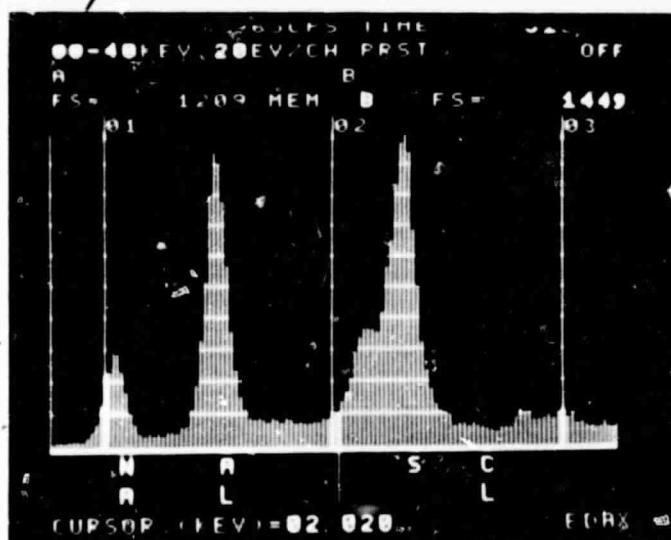
NaCl PARTICLE AND Al_2O_3 SUBSTRATE EXPOSED TO AIR AND 0.2% SO_2 AT
 600°C . FOR FOUR HOURS.

FIGURE 13



X 4250

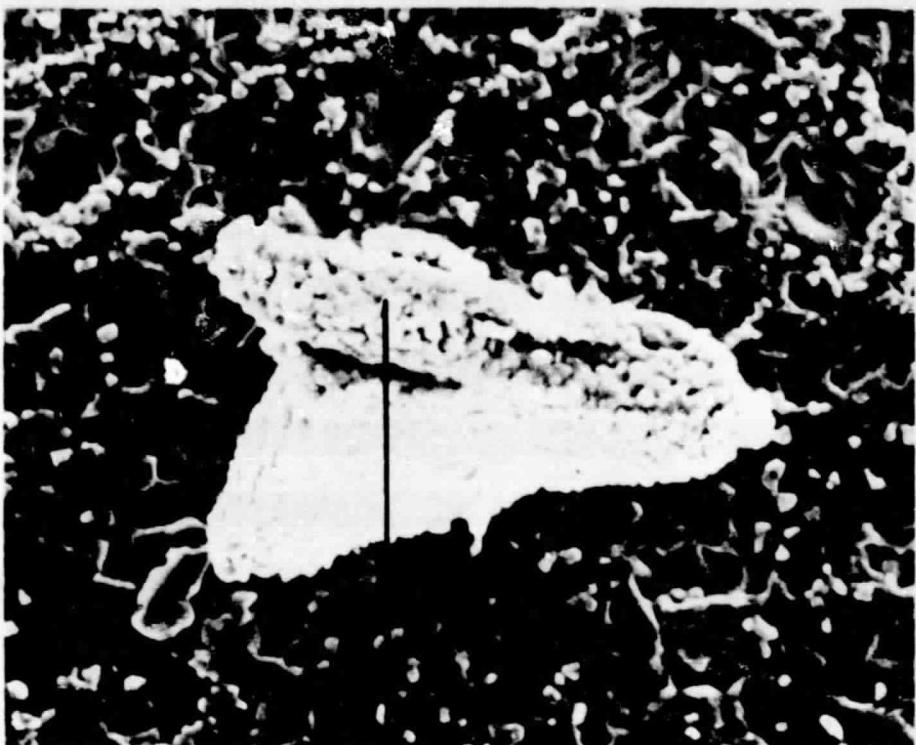
EDAX OF NaCl PARTICLE:
HIGH SULFUR PEAK



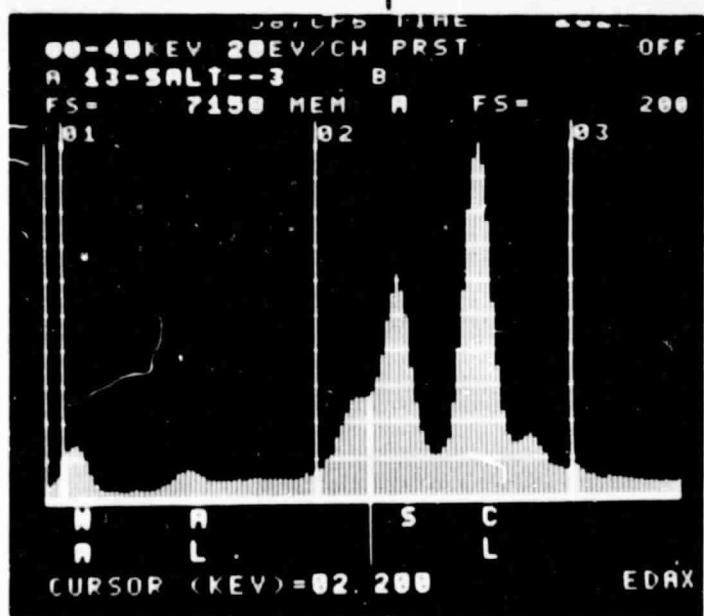
EDAX OF Al_2O_3 SUBSTRATE:
LOWER SULFUR CONTENT THAN
THAT IDENTIFIED ON
THE NaCl PARTICLE.

Al_2O_3 SUBSTRATE IN THE VICINITY OF THE NaCl PARTICLES AFTER EXPOSURE
TO AIR AND 0.2% SO_2 AT 600°C . FOR FOUR HOURS.

FIGURE 14



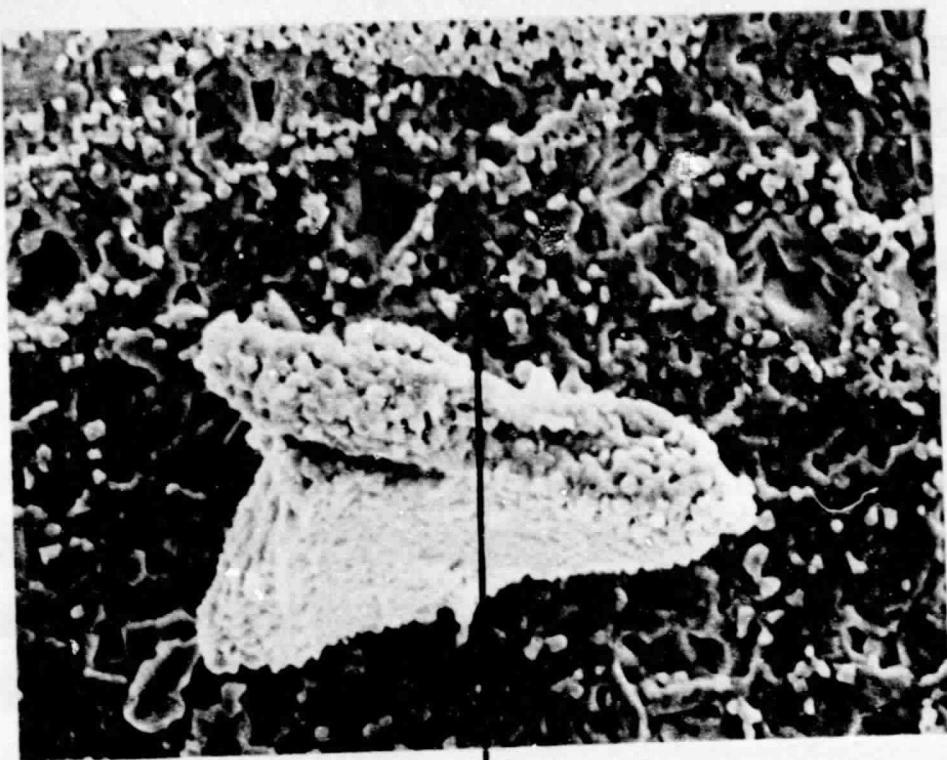
X 730



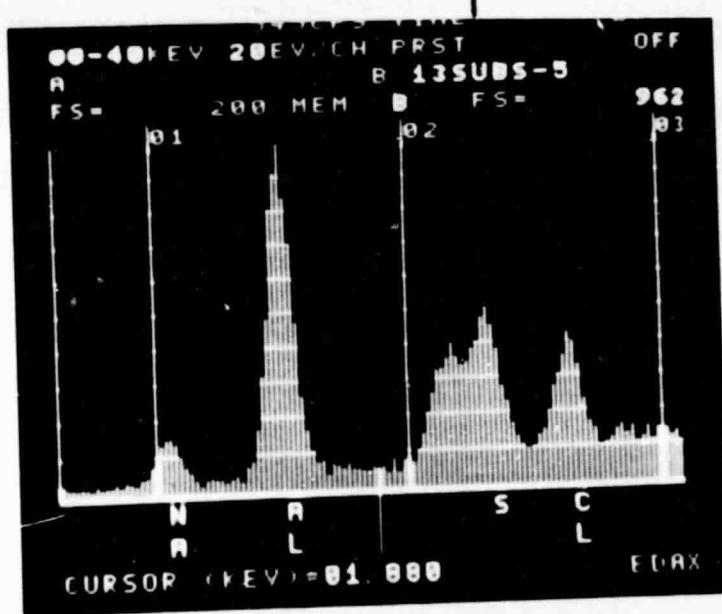
EDAX OF NaCl PARTICLE:
CHLORINE AND SULFUR PRESENT.

NaCl PARTICLE EXPOSED TO AIR PLUS 0.99% SO_2 AT 600°C . FOR 10 MINUTES.

FIGURE 15



X 700



EDAX OF NaCl PARTICLE:
HIGH SULFUR PEAK.

NaCl PARTICLES EXPOSED TO AIR AND 0.99% SO₂ AT 600° C. FOR 10 MINUTES.

FIGURE 16

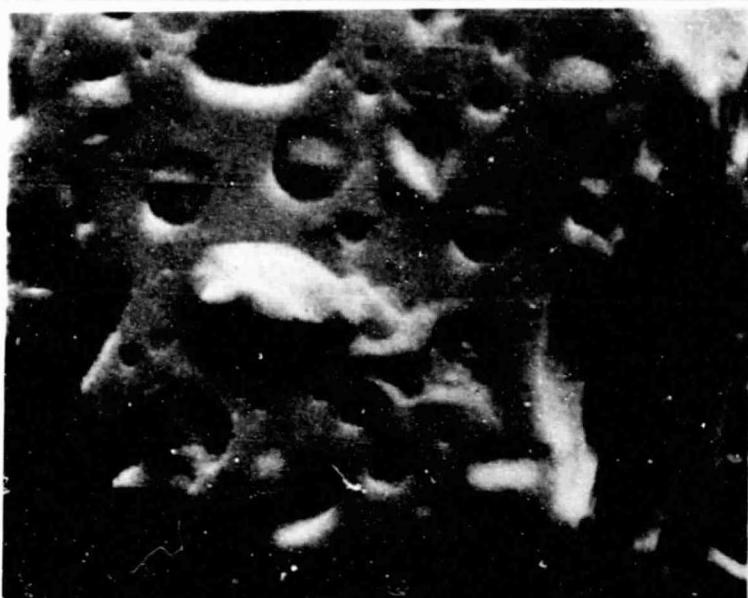
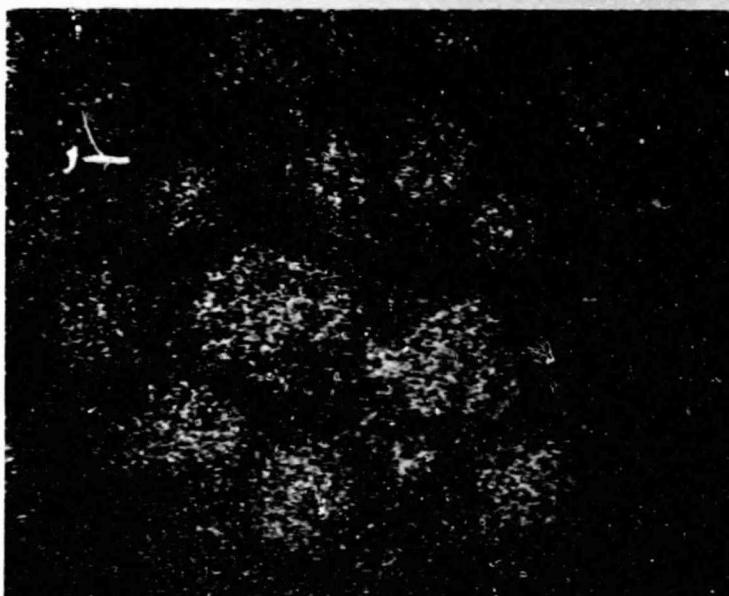


FIGURE 17
NaCl PARTICLE EXPOSED TO AIR
AND 0.99% SO₂ AT 600° C. FOR
10 MINUTES.

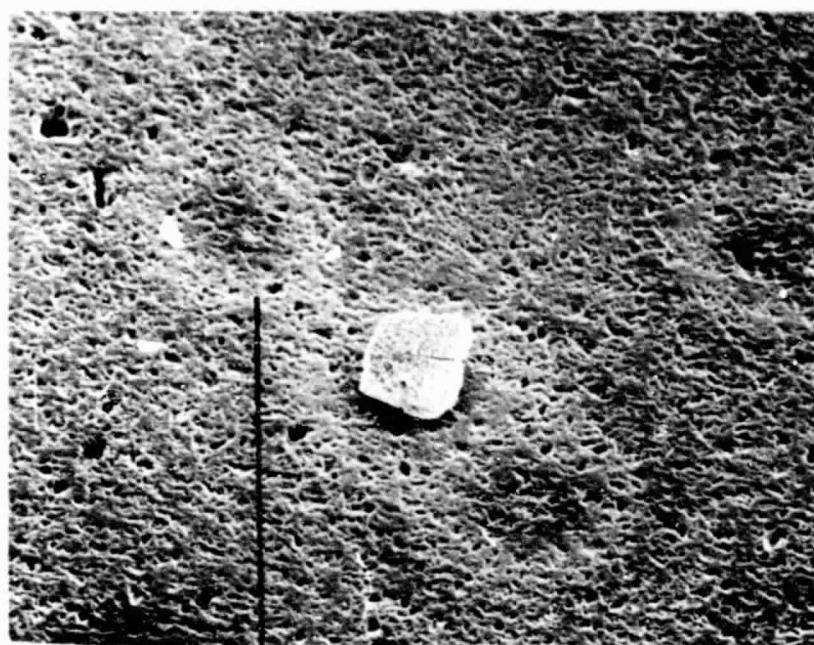
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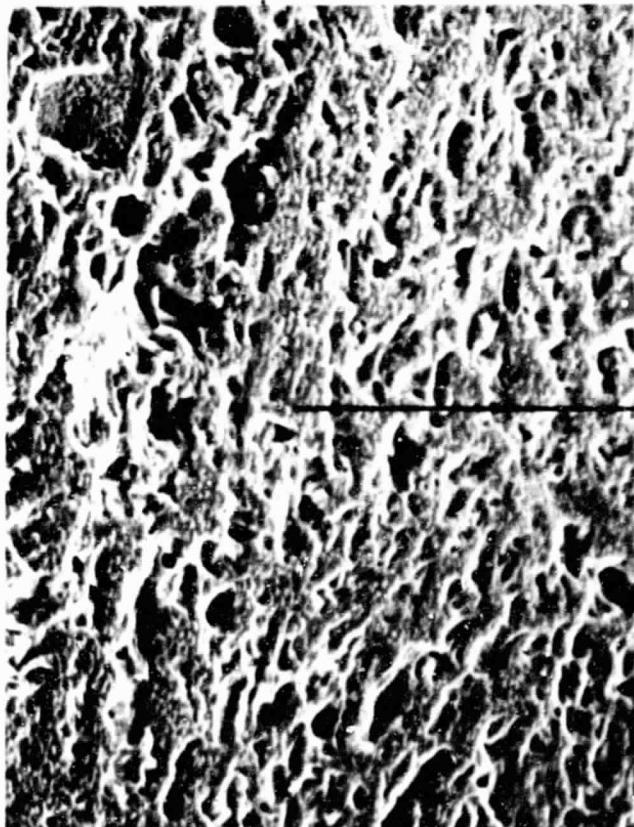
SULFUR IMAGE OF ABOVE PHOTO.



CHLORINE IMAGE OF ABOVE PHOTO.

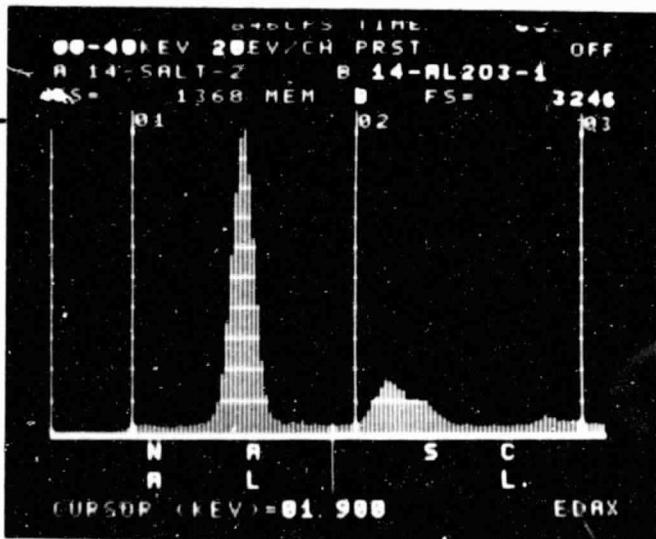


a.) X 150

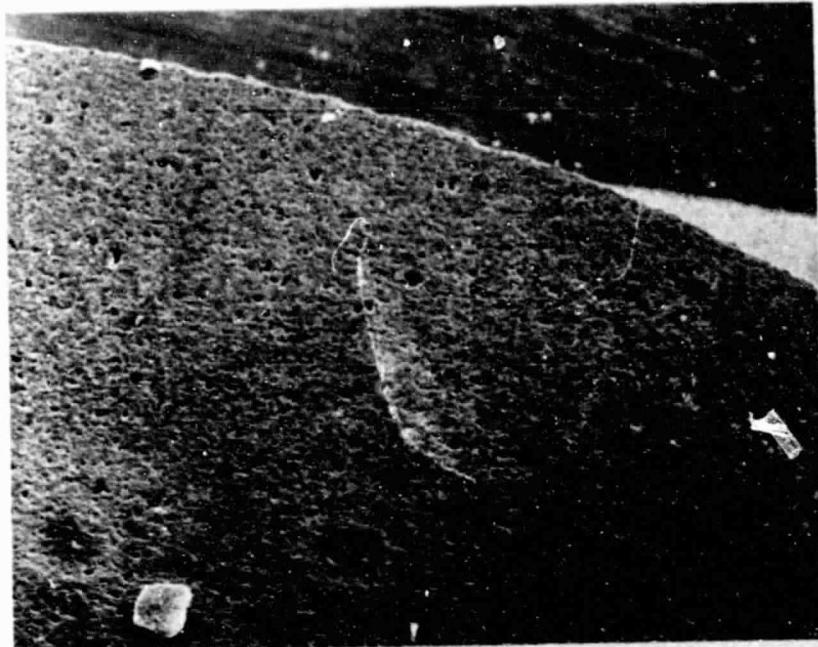


b.) X 750

EDAX OF Al_2O_3 SUBSTRATE;
SULFUR PEAK INDICATED.

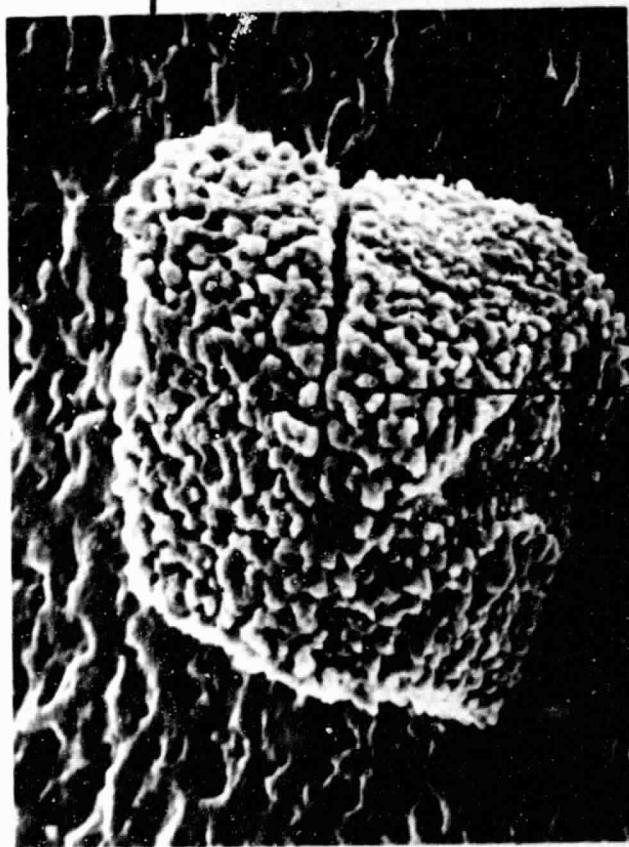


NaCl PARTICLES EXPOSED TO AIR AND 0.99% SO_2 AT 600^0C . FOR 30 MINUTES.
FIGURE 18



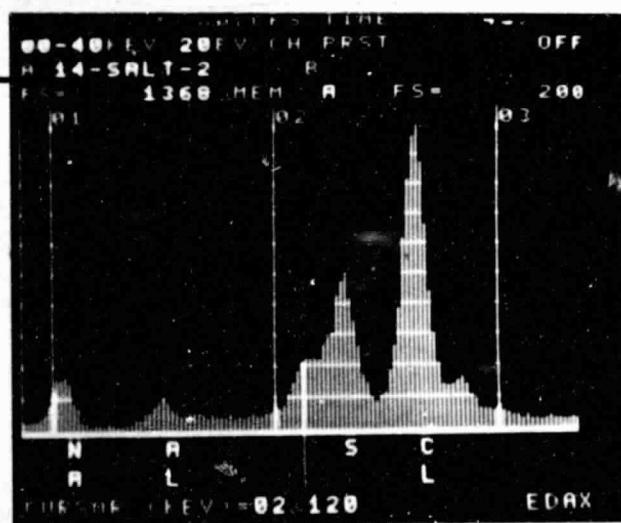
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a.) X 70



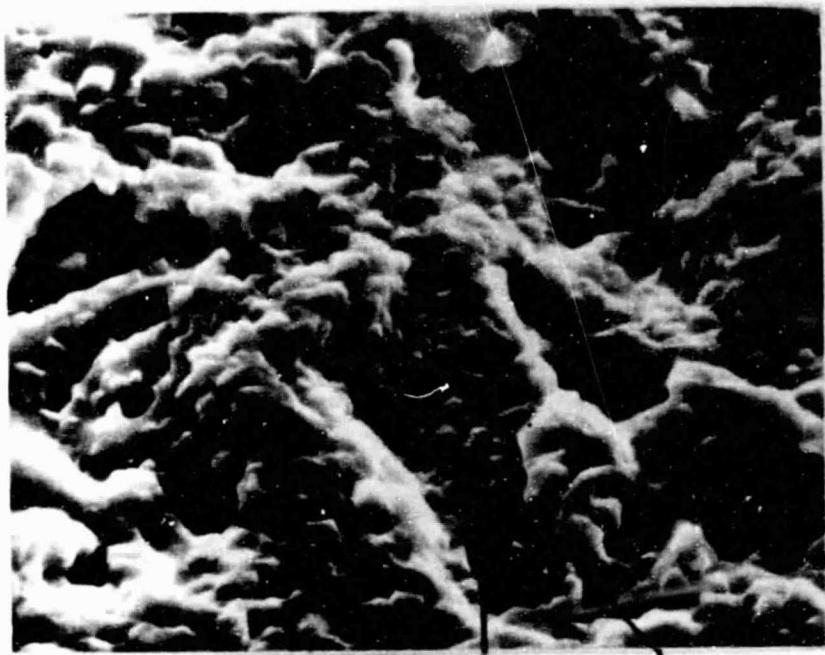
b.) X 750

EDAX OF NaCl PARTICLES;
SULFUR PEAK PRONOUNCED.

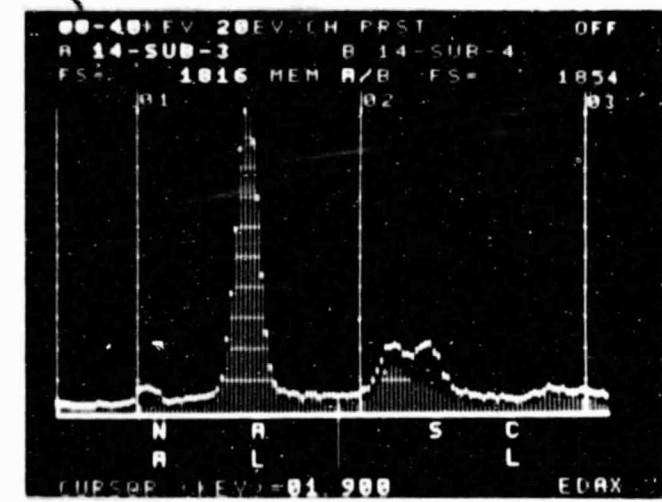


NaCl PARTICLES EXPOSED TO AIR AND 0.99% SO₂ AT 600° C. FOR 30 MINUTES.

FIGURE 19



a.) X 3700

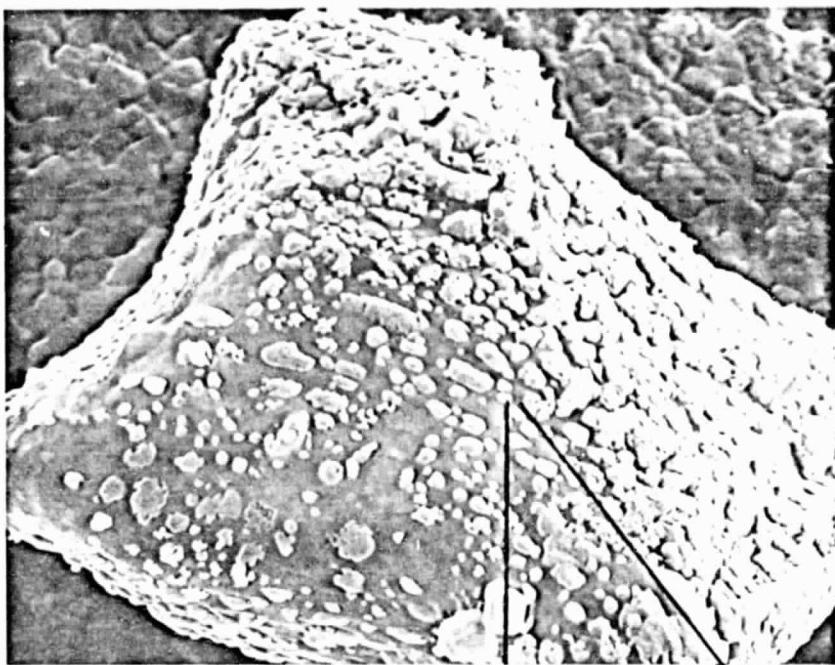


EDAX OF Al_2O_3 SUBSTRATE;
SULFUR CONTENT PRESENT.

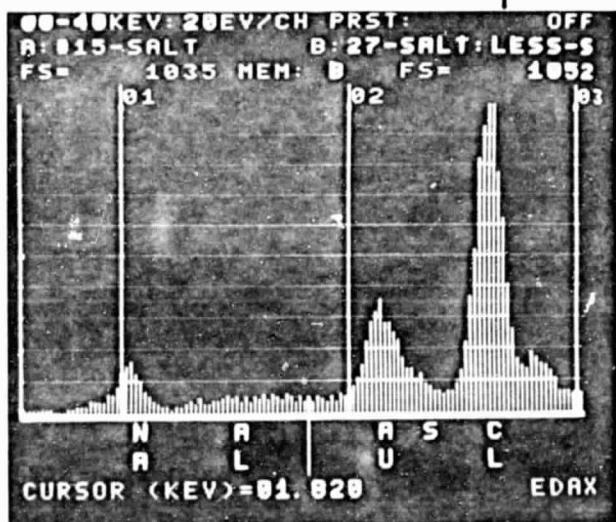
b.) X 14000

Al_2O_3 SUBSTRATE EXPOSED TO AIR AND 0.99% SO_2 AT 600°C . FOR 30 MINUTES.

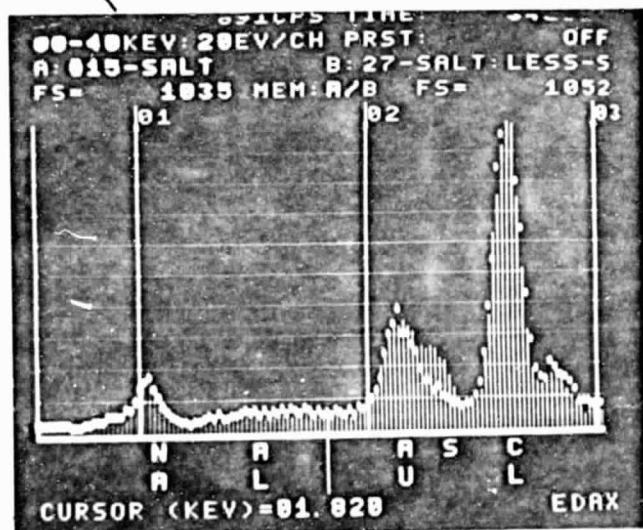
FIGURE 20



X 1400



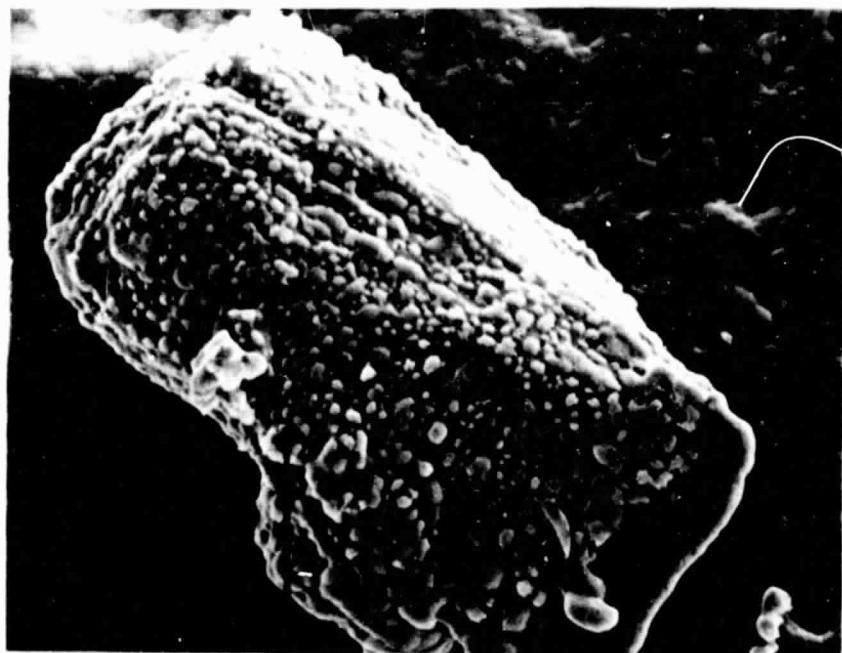
EDAX OF NaCl PARTICLE;
SULFUR PRESENCE INDICATED.



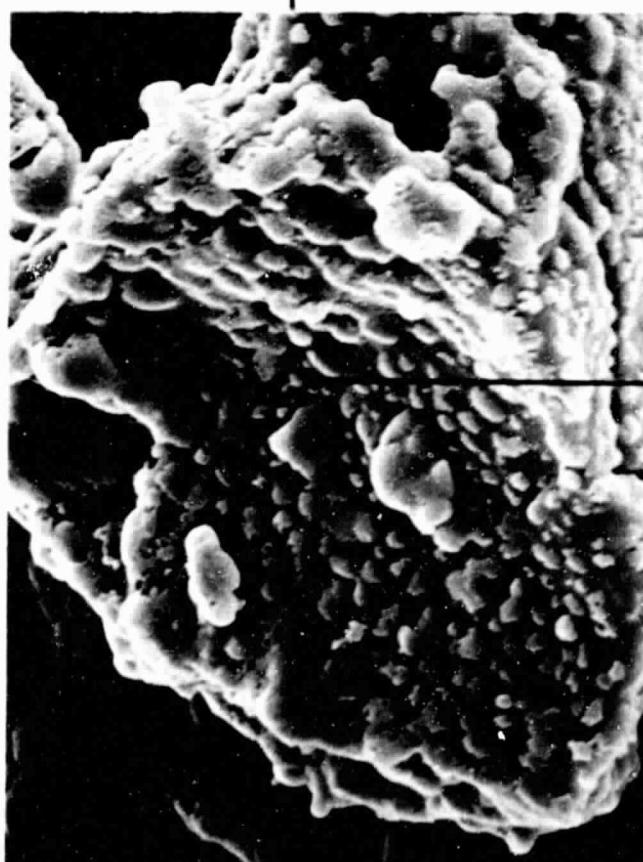
EDAX OF NaCl PARTICLE;
SULFUR PRESENCE INDICATED.

NaCl PARTICLES EXPOSED TO AIR AND 0.99% SO₂ AT 600° C. FOR ONE HOUR.

FIGURE 21

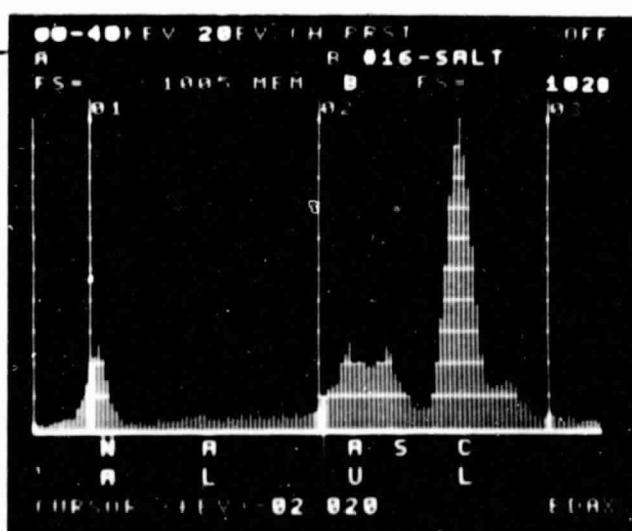


a.) X 700



b.) X 1600

EDAX OF NaCl PARTICLE;
TRACE EVIDENCE OF SULFUR.



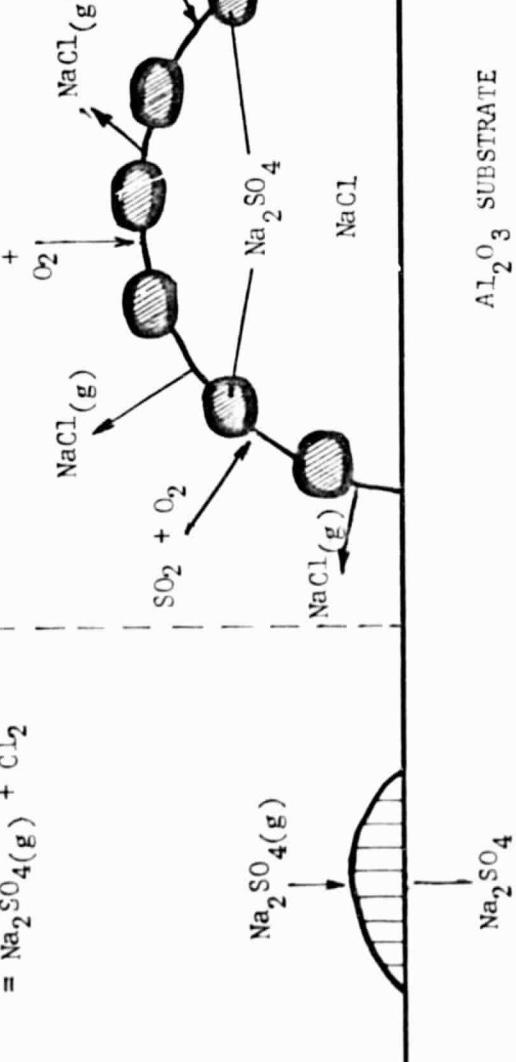
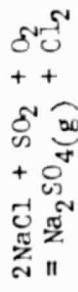
NaCl PARTICLE EXPOSED TO AIR AND 0.99% SO₂ AT 600 °C. FOR FOUR HOURS.
2

FIGURE 22

Na_2SO_4 deposition
following reaction
in gas phase.

Formation of Na_2SO_4 on NaCl particle
with simultaneous NaCl evaporation.

Na_2SO_4 formation by
direct reduction on
substrate surface.



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FIGURE 23. DIAGRAM OF POSSIBLE MECHANISMS INVOLVED IN THE CONVERSION OF NaCl TO Na_2SO_4 ,
ON AN ALUMINA SUBSTRATE, IN THE ABSENCE OF LIQUID FORMATION. 500-600°C.